Role of Hf on phase formation in $Ti_{45}Zr_{38-x}Hf_xNi_{17}$ liquids and solids

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Hafnium and zirconium are very similar, with almost identical sizes and chemical bonding characteristics. However, they behave differently when alloyed with Ti and Ni. A sharp phase formation boundary near 18-21 at.% Hf is observed in rapidly-quenched and as-cast $Ti_{45}Zr_{38-x}Hf_xNi_{17}$ alloys. Rapidly-quenched samples that contain less than 18 at.% Hf form the icosahedral quasicrystal phase, whiles samples containing more than 21 at.% form the 3/2 rational approximant phase. In cast alloys, a C14 structure is observed for alloys with Hf lower than the boundary concentration, while a large-cell (11.93 Å) FCC Ti_2Ni-type structure is found in alloys with Hf concentrations above the boundary. To better understand the role of Hf on phase formation, the structural evolution with supercooling and the solidification behavior of liquid $Ti_{45}Zr_{38-x}Hf_xNi_{17}$ alloys (x=0, 12, 18, 21, 38) were studied using the Beamline Electrostatic Levitation (BESL) technique using 125keV x-rays on the 6ID-D beamline at the Advanced Photon Source, Argonne National Laboratory. For all liquids primary crystallization was to a BCC solid solution phase; interestly, an increase in Hf concentration leads to a decrease in the BCC lattice parameter in spite of the chemical similarity between Zr and Hf. A Reitveld analysis confirmed that as in the cast alloys, the secondary phase that formed was the C14 below the phase formation boundary and a Ti_2Ni-type structure at higher Hf concentrations. Both the liquidus temperature and the reduced undercooling change sharply on traversing the phase formation boundary concentration, suggesting a change in the liquid structure. Structural information from a Honeycutt-Anderson index analysis of reverse Monte Carlo fits to the S(q) liquid data will be presented to address this issue.
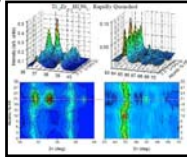
Role of Hf on Phase formation in Ti45Zr38-xHfxNi 17 $Ti_{45}Zr_{(38-x)}Hf_xNi_{17}$ Liquids and Solids

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Introduction

● Initial studies revealed a sharp boundary in phase formation around 21 at% Hf (x=21) in the Ti45Zr(38-x)HfxNi17 system. In quenched alloys the i-phase forms below the boundary, while a 3/2 rational approximant to the quasicrystal forms above. In cast alloys, the C14 Laves phase forms below and a Ti2Ni-type (cF96) forms above. Further study of the liquid structure and evolution and the influence of Hf on phase formation and physical properties were studied using the Bamline Electro-Static Levitation (BESL) technique [1]

Experimental methods
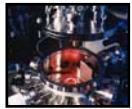
The BESL apparatus (left) and schematic diagram (right); adapted from [1]
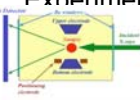
● Containerless, high vacuum processing
● Synchrotron XRD throughout entire phase spectrum (incl. supercooled liquid)
● 125 keV X-ray beam; 6ID-D beamline, Advanced Photon Source, Argonne National Laboratory
● Primary crystallization to BCC solid solution (beta); remaining liquid crystallizes to C14 or cF96
● Remarkable supercooling wrt beta phase indicates an increased barrier to nucleation due to structural differences between liquid and solid
● Frank's hypothesis supposes icosahedral order in liquid metals to account for nucleation barrier [2]

$$T_{rl} = \frac{(T_l - T_r)}{T_l}$$
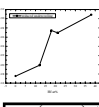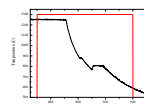
Structural studies

● High resolution scattering data collected to 14.5 inverse Å
● S(q) and g(r) generated by PDFgetX2 software [3]
● Evolution of g(r) at constant reduced temperature indicates local expansion (1st neighbor) and expansion then contraction upon traversing phase formation boundary at 2nd neighbor distances

● What effects are causing the structural changes at near and extended length scales?
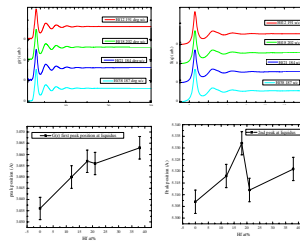
● Electron configurations:
Zr: $[Kr]4d^25s^2$
Hf: $[Xe]4f^{14}5d^26s^2$
● Observed contraction of beta BCC lattice due to stronger bonding of 5d electrons in Hf
● Intermediate phases index to C14 (hexagonal) structure and cF96 (FCC) structure with residual beta
● C14 lattice parameters
a = 5.285 Å
c = 8.560 Å
packing frac. = 0.575
● cF96 lattice parameters
a = 11.92 Å
packing frac. = 0.565
● Crystal images adapted from [4]
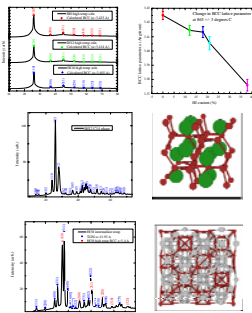
Physical

● Liquid density measured during levitation using a photographic technique with droplet edge-fitting [5]
● Normalized density, coefficient of thermal expansion peaked at boundary composition
● Heat of mixing for a regular solution

$$G_{mix} = H_{mix} + TS_{mix}$$

● Estimates of the enthalpy of mixing favor mixing of Ni-Hf below the phase boundary; Ni-Zr above
● Atomic volumes (cm^3/mol)
Ti: 10.6 Zr: 14.1 Hf: 13.6 Ni: 6.6
● In cooling liquids below the phase boundary, Hf will tend to mix with Ni and Ti in the inner shell, above the boundary Zr is more likely
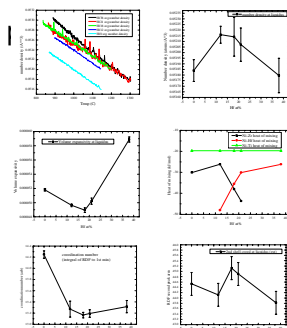
Structural simulation results
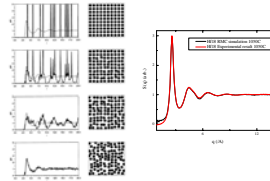
structure generation from RMC; adapted from [7]

● Reverse Monte Carlo (RMC) simulation generates atomic configuration [7]
● Rejection sampling algorithm using quality of fit (chi square) as analogy to energy in Metropolis Monte Carlo (MMC)
● RMC reveals random arrangement of Zr and Hf generates best agreement to experimental data

Quantifying structure

root pair (white circles) and neighbors; adapted from [8]
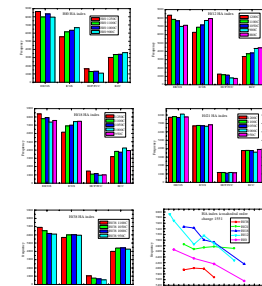
● Honeycutt-Andersen (HA) index [8] and Bond Orientational Order parameter [9] (BOO) analyses used to quantify order in the RMC structures
● HA index describes bonded neighbors of a root pair, i.e.

1 5 5 1

diagram type / no. near neighbors / no. bonds / placeholder
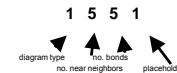
● Icosahedral or distorted icosahedral order is most prominent for all compositions
● Local icosahedral order is increasing with supercooling below phase boundary (x ≤ 18); roughly constant above
● Local icosahedral order more prominent in mixed Zr-Hf than in endpoints

● Effect of Hf above the phase formation boundary is to suppress the tendency to increase local icosahedral order with cooling; system is effectively jammed

● BOO parameter uses quadratic and third order invariants formed from bond spherical harmonics to quantify order

$$Q_{lm}(\vec{r}) \equiv Y_{lm}(\theta(\vec{r}),\phi(\vec{r}))$$

$$Q_l = \left[\frac{4\pi}{2l+1}\sum_{m=-l}^{l}|\bar{Q}_{lm}|^2\right]^{1/2}$$

● Characteristic distribution of Ql's identify cluster types
● 13 atom icosahedral, fcc, and hcp; 15 atom bcc and 7 atom simple cubic
● Icosahedral order is most prominent in all and little change is observed with supercooling

cluster figures adapted from [9]

● HA and BOO are describing only dynamics of the local order, and are not capturing the dynamics at longer length scales

Conclusions

● Remarkable undercooling has been observed, and can be attributed to increasing mismatch of undercooled liquid and BCC solid solution, due to increasing bond strength of Hf.
● Local cluster size is expanding with increased Hf due to strain effects, while extended cluster size changes dramatically upon traversing phase boundary
● Below the boundary icosahedral order increases, allowing i-phase formation in quenching; above the boundary the local order is jammed allowing formation of the 3/2 RA
● Chemical effects, heats of mixing, cluster dynamics

References and acknowledgments

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